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REPORT NO. NADC-87016-60

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DEVELOPMENT OF A PRIMER/TOPCOAT AND FLEXIBLE PRIMER FOR ALUMINUM

AD-A182 132

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20 MARCH 1987

PHASE REPORT
Project No. R534A52
Work Unit ZM 540

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JUN 25 1987
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20030128004

Prepared For
NAVY EXPLORATORY DEVELOPMENT PROGRAM
AIRBORNE MATERIALS
(NA2A)
NAVAL AIR DEVELOPMENT CENTER
Warminster, PA 18974-5000

87 6 24 003

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SECURITY CLASSIFICATION OF THIS PAGE

A 182132

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b. RESTRICTIVE MARKINGS N/A		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for Public Release; Distribution unlimited		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) NADC-87016-60			5. MONITORING ORGANIZATION REPORT NUMBER(S) N/A		
6a. NAME OF PERFORMING ORGANIZATION Naval Air Development Center		6b. OFFICE SYMBOL (If applicable)		7a. NAME OF MONITORING ORGANIZATION N/A	
6c. ADDRESS (City, State, and ZIP Code) Warminster, PA 18974-5000				7b. ADDRESS (City, State, and ZIP Code) N/A	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Navy Exploratory Materials Pgm		8b. OFFICE SYMBOL (If applicable)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N/A	
8c. ADDRESS (City, State, and ZIP Code) Naval Air Development Center Warminster, PA 18974-5000		10. SOURCE OF FUNDING NUMBERS			
		PROGRAM ELEMENT NO.		PROJECT NO. R534A52	TASK NO.
				WORK UNIT ACCESSION NO. ZM 540	
11. TITLE (Include Security Classification) (U) Development of a Primer/Topcoat and Flexible Primer for Aluminum					
12. PERSONAL AUTHOR(S) Charles R. Hegedus					
13a. TYPE OF REPORT Phase		13b. TIME COVERED FROM Oct 84 to Sep 86		14. DATE OF REPORT (Year, Month, Day) 1987, March 20	
15. PAGE COUNT					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
			Corrosion Protection Flexible Primer		
			Organic Coating Sealant		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Two corrosion preventive organic coatings have been developed for use on aluminum and specifically for application on Navy aircraft. They provide two alternatives for improving aircraft paint systems. The first coating can be applied directly to an aluminum substrate and perform as a self-priming topcoat. It consists of a two component, aliphatic polyurethane binder with titanium dioxide, zinc molybdate, zincophosphate, an organo-zinc salt, and titanium dioxide vesiculated bead pigments. This primer/topcoat meets or exceeds all of the critical performance requirements of the current Navy aircraft paint system, Mil-P-23377 epoxy primer and Mil-C-83286 polyurethane topcoat. It exhibits good adhesion, corrosion inhibition, flexibility, chemical and weather resistance. The primer/topcoat has been formulated in lusterless gray colors common on Navy tactical aircraft. The volatile organic content (VOC) of the primer/topcoat prior to thinning is 395 grams of organic solvent per liter of paint. The VOC after thinning with 1,1,1 trichloroethane, which is currently an exempt solvent, to a viscosity compatible with conventional air spray, is 295 grams per liter. This is well within the current maximum limit set by South Coast Air Quality Control District Rule 1142 for aerospace equipment, 420 g/l. The use of this coating will reduce: (continued on reverse)					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a. NAME OF RESPONSIBLE INDIVIDUAL Charles R. Hegedus			22b. TELEPHONE (Include Area Code) 215-441-1452		22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE

U.S. Government Printing Office: 1986-638-612

0102-LF-014-6602

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19. ABSTRACT (continued)

- 1. Paint application and removal time and manpower
- 2. Aircraft weight
- 3. Aircraft downtime and
- 4. Volatile organic component (VOC) and chromate emissions

The second coating is a flexible primer which was developed using the above polyurethane binder. It contains strontium chromate, zinc chromate, barium chromate, and zinc molybdate corrosion inhibiting pigments. This primer meets or exceeds all of the performance requirements of Mil-P-23377 and has significantly more flexibility. Aluminum specimens coated with the NADC flexible primer remained in 5% salt spray for one year without any corrosion of the aluminum or damage to the coating. The NADC flexible primer can be used to increase the flexibility of a coating system and reduce the risk of paint cracking and substrate exposure. The VOC of the flexible primer prior to thinning is 442 grams of solvent per liter of paint. After thinning to conventional air spray viscosity with 1,1,1 trichloroethane, the VOC is 294 grams per liter which is well below the Rule 1142 limit of 350 g/l for aerospace equipment.

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Availability Codes	
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1.0 INTROEUCTION

The objective of the investigation discussed herein was to develop a coating which could be applied directly to an aluminum substrate and also perform as a topcoat. In addition to developing this primer/topcoat, a flexible primer was formulated to improve the flexibility of the current Navy aircraft coating system.

U.S. Navy aircraft currently are painted with a high performance protective paint system consisting of an epoxy primer (MIL-P-23377 or MIL-P-85582) and a polyurethane topcoat (MIL-C-83286). Several types of aircraft also require a coat of spray sealant (MIL-S-8802, MIL-S-81733, or MIL-P-87122) between the primer and topcoat. The current paint system was designed to protect aluminum aircraft structures from the harsh aircraft carrier environment which contains corrosive sea water spray and, on non-nuclear powered carriers, sulfur dioxide stack gases. The epoxy primers are adherent and inhibit corrosion of the substrate. The polyurethane topcoat is chemical and weather resistant, flexible, and provides the desired optical properties. A sealant coat is occasionally applied to enhance the flexibility of the coating system and prevent cracking of the paint, especially around fasteners.

Although the current paint system performs well, the individual coatings exhibit several deficiencies. The primer is brittle, especially at low temperatures (-60° F), resulting in extensive cracking of the paint system in highly flexed areas of the aircraft. The sealants are soft and easily deformed and are difficult to apply and remove. In addition, increased awareness and concern for the environment and worker safety have caused local and state governments to limit volatile organic component (VOC) emissions from painting operations. These regulations have impacted Naval Air Rework Facilities (NARFs) and original equipment manufacturers (OEMs) by limiting the amount and types of paint which can be applied. Numerous facilities have been threatened with fines and closure for using the above paint system. The carcinogenic effects of chromates which are used in aircraft primers (Mil-P-23377 and Mil-P-85582) present another concern with current coating systems. Use of chromates has not been restricted to date but limiting regulations are expected in the near future.

The use of one coating, a primer/topcoat, which is adherent, corrosion inhibiting, flexible, chemical and weather resistant, will provide performance, time, and money-saving improvements. Application of one flexible coating reduces the risk of coating failure due to cracking and allows easy touch-up when required. Application of a primer/topcoat to replace two coatings decreases the amount of VOC emissions during the painting operation. In addition, the coatings developed during this effort were specifically formulated with the intent of minimizing VOC and eliminating chromates. Other advantages of the primer/topcoat are the amount of time and manpower saved when applying and removing the system. The current paint system requires the application of a primer and topcoat over the entire exterior surface of the aircraft and application of a spray sealant over certain designated areas. The primer/topcoat would permit the application of only one coating over the aircraft, thus reducing application time by at least 50%. In addition, the time required and the cost to strip the paint from the aircraft when rework is required would be significantly reduced. The use of a primer/topcoat would reduce the weight of the paint system on the external surface of an aircraft by

30 to 40%. For an F-14, this would be a weight reduction of approximately 55 pounds.

The initial objective of this investigation was to develop the primer/topcoat coating. During development, it became apparent that a flexible primer could be formulated using a similar binder and pigment system. The use of this primer would require the application of a conventional topcoat. The advantage of a flexible primer is elimination of the need for a sealant coat while improving the overall flexibility of the paint system. This also would decrease application time and coating system weight by eliminating the need for a sealant coat. Reference (1) discusses an evaluation of elastomeric primers and sealants for use on aircraft.

Although the primer/topcoat and flexible primer both were designed for use on Navy aircraft, they would not be used in conjunction. The advantages of both coatings are discussed above and although use of the primer/topcoat would be more beneficial, until extensive field testing is completed, full scale use cannot be recommended. Therefore, introduction of both coatings provides two alternative approaches to improve aircraft coating systems.

2.0 COATING PREPARATION AND EXPERIMENTAL PROCEDURES

During the three phases of coating development, paints were prepared and applied to aluminum panels for optical and physical testing. The formulated coatings were prepared in the following manner. The designated pigments were mixed with the desired resin system in a one quart glass jar half filled with glass shot (5 millimeters in diameter). This mixture was vigorously agitated on a paint shaker for approximately 30 minutes. The required fineness of grind of the pigment was a minimum of 5 according to ASTM D1210 using a Hegmen gauge.

Following pigment milling and dispersion in the resin system, this mixture was added to the appropriate curing agent when necessary. The viscosity of the formulated coating was measured using a Zahn #2 cup. A viscosity ranging from 18 to 22 seconds was desired for application of the coating. If viscosity reduction was required, the admixed material was diluted with solvent specified by the resin manufacturer or appropriate substitutes. The resulting coatings were applied to aluminum specimens of 3.0 x 6.0 x 0.02 inches (7.62 x 15.24 x 0.05 cm) using conventional air spray. The specimens used in all tests, except the flexibility and filiform corrosion tests, were 2024-T3 bare aluminum alloy meeting specification QQ-A-250/4. The specimens were cleaned and chromated with materials conforming to MIL-C-81706 to produce a chemical conversion coating meeting MIL-C-5541. The filiform test specimens were 2024 - T3 Alclad chromate conversion coated per Mil-C-5541. The flexibility test specimens were 2024-0 temper aluminum alloy, anodized in accordance with MIL-A-8625, type 1.

While under development, the formulated coatings were tested against each other for comparison and illustration of the best formulation. When the optimum formulations were determined, they were tested against control materials, MIL-P-23377E epoxy primer and MIL-C-83286 polyurethane topcoat. Although the current revision of Mil-P-23377 is the "D" version, the "E" revision has been drafted. A control primer meeting the "E" revision requirements was used as a control in this study. Koroflex, a one-component, flexible primer manufactured by DeSoto, Inc. was used as the control for the flexible primer materials. The

conventional primers were applied to a thickness of 0.9 mils (22.9 μ m). Flexible primers were applied to a thickness of 1.1 to 1.5 mils (27.9 to 38.1 μ m). The conventional topcoats were applied one hour following primer application to a thickness of 1.8 to 2.0 mils (45.7 to 50.8 μ m). The primer/topcoats were applied to film thickness of 2.0 to 2.2 mils (50.8 to 55.9 μ m). In all tests, the primers were analyzed without a topcoat; for adhesion and corrosion, they also were tested with a topcoat. All coatings were allowed to cure for 7 days at ambient laboratory conditions prior to testing.

The set-to-touch time was measured as the time following application when the coating clung weakly to the finger when touched under gentle pressure, but none of the film transferred to the finger. The dry-hard time of the coatings was measured according to Method 4061 of Federal Test Method Standard 141b.

The method was performed by placing the coated panel between the thumb and forefinger, with the thumb on the coating, and applying maximum pressure. The impression left on the coating was then lightly polished with a soft cloth. The dry-hard time was recorded as the time following application when the impression left by the thumb could be completely removed.

The 60 and 85 degree gloss was measured according to ASTM Method D523 using a GG-7562 multi-angle glossmeter manufactured by Gardner Laboratory. Color of the primer/topcoats was characterized by measuring tristimulus and LAB values using the McBeth 1010S colorimeter with illuminant C.

Adhesion of the coating systems was measured by wet-tape test defined in ASTM D3359, Method A and the Scrape-Adhesion Test defined in ASTM D2197, Method B. The Wet-Tape Test was performed by immersing a coated specimen in distilled water at 75 \pm 5 $^{\circ}$ F (24 \pm 3 $^{\circ}$ C) for 24 hours. Upon removal, two parallel cuts were made, one inch apart, through the coating and into the substrate. Using firm pressure, a one-inch wide strip of 3M-250 masking tape (manufactured by Minnesota Mining and Manufacturing Company) was placed on the coating perpendicular to the direction of the cuts. Following this, the tape was removed in a quick and steady pull. The coating was then inspected and evaluated in accordance with the following system:

- 5A No peel or removal
- 4A Trace peeling or removal along the cut
- 3A Jagged removal along cuts up to 1/16 inch (1.6mm) on either side
- 2A Jagged removal along most of the cuts up to 1/8 inch (3.2mm) on either side
- 1A Removal from over 50% of the area under the tape
- 0A Removal of all the coating under the tape and/or beyond the tape

The adhesion of the primers and primer/topcoats to the substrate and the intercoat adhesion between the topcoats and the primer were evaluated using the SG-1605 Scrape-Adhesion Test Apparatus manufactured by Gardner Laboratory. The test was performed by guiding a weighted stylus at a 45-degree angle to the specimen along the substrate into the coating being tested. The scrape-adhesion was recorded as the heaviest weight used without the stylus shearing the coating from the underlying surface. For primers and primer/topcoats, this surface was the aluminum substrate, for topcoats, it was the primer coat.

The coatings were tested for resistance to hydraulic fluids conforming to

specifications MIL-H-5606, MIL-H-83282, and MIL-H-83306 Monsanto Skydrol 500B and a lubricating oil conforming to Specification MIL-L-23699. Coated specimens were immersed in the MIL-H-5606 and MIL-H-83282 hydraulic fluids at 150° F (66° C) for 24 hours, in MIL-L-23699 lubricating oil at 250° F (121° C) for 24 hours, and in MIL-H-83306 hydraulic fluid at 70° F (21° C) for 7 days. Upon removal, the coatings were examined for softening, blistering, loss of adhesion, and any other coating defects.

Salt-spray tests were conducted according to ASTM Method B117. Specimens were scribed with an "X" through the coating system and into the substrate prior to the exposure period. Although the specified exposure period for Mil-P-23377E and Mil-C-83286B are 1000 and 500 hours, respectively, additional specimens were exposed for 2000 hours and for one year. The specimens were subsequently examined for corrosion deposits in the scribe and blistering and uplifting of the coating.

Additional salt spray tests were performed using a specimen consisting of an aluminum panel attached to a graphite/epoxy composite as illustrated in Figure 1. A 6 x 6 x 0.125 inch (15.24 x 15.24 x 0.32 cm) aluminum specimen conforming to QQ-A-250/12 (T6 temper), anodized per Mil-A-8625, Type I was primed. Two diagonal intersecting scribes were made through the primer and into the substrate. A 3 x 3 x 0.09 inch (7.62 x 7.62 x 0.24 cm) graphite/epoxy panel with 0, 90 orientation of approximately 16 plies was attached to the center of the aluminum specimen with four nylon fasteners. Four 2 inch lines were scribed along the edge of the composite into the aluminum. The specimen was then exposed to 5 % salt spray for 500 hours, removed, disassembled and analyzed for coating defects and corrosion of the aluminum.

The filiform corrosion test was performed by scribing an "X" through the applied coating and into the aluminum substrate. The panel was then placed in a desiccator approximately 2 inches above concentrated (12 normal) hydrochloric acid for 65 minutes. Without rinsing the specimen, it then was placed in a chamber at 102° F (39° C) and 80 percent relative humidity for 1000 hours. The specimens were then examined for deformities in the coating and corrosion of the aluminum, especially thread like defects in the film stemming from the scribe.

The coatings were evaluated for strippability by placing a painted specimen at a 60° angle with the horizontal. Mil-R-81294 paint remover was poured along the upper edge to completely cover the surface. After 15 minutes, the specimen was brushed and rinsed with water, removing the loosened coating. The area of the specimen in which the coating was removed was recorded.

Humidity resistance tests were performed by exposing painted specimens to 95% relative humidity and 120° F (49° C) for 30 days. The coatings were then examined for blistering, softening, and loss of adhesion.

The coating systems were tested for flexibility according to ASTM Method D1737. Specimens at -60° F (-51° C) were bent around 1/8, 1/4, 1/2, and 1 inch mandrels. After returning to room temperature, the coating systems were examined for cracking along the bend.

The coating systems were tested for impact flexibility as defined in Method 6226 of Federal Test Method Standard 141B. The test instrument consisted of a solid steel cylinder with spherical knobs protruding from the end. These knobs

were designed such that the coating system could be subjected to elongations of 0.5, 1, 2, 5, 10, 20, 40, and 60 percent. The steel cylinder was allowed to fall freely from a height of 42 inches (1.05 meters) through a hollow guide cylinder, striking the reverse side of a coated specimen. The imprints formed from the knobs were then examined for cracking. The imprint causing the highest elongation which did not cause cracking of the coating was recorded as the impact flexibility.

Painted specimens were exposed for 500 hours in a 6000-watt, xenon-arc weatherometer. The continuous cycle consisted of 102 minutes of high-intensity light only and 18 minutes of light and water spray. The specimens were tested according to ASTM Method G26, Type BF with the conditions in the chamber as follows:

Black body temperature	$140 \pm 5^\circ \text{ F} (60 \pm 3^\circ \text{ C})$
Relative humidity	$50 \pm 5\%$
Intensity of the xenon arc	0.55 ± 0.05 watts per square meter at 340 nanometers wavelength

After 500 hours exposure, the specimens were examined for substrate corrosion and coating color, gloss, and impact flexibility changes. Although Mil-C-83286B specifies the use of a carbon-arc weatherometer, the xenon-arc exposure has been demonstrated to be as severe.

The topcoats were tested for heat resistance by subjecting coated specimens to $400^\circ \text{ F} (149^\circ \text{ C})$ for four hours. The coatings were then examined for changes in color, gloss, and impact flexibility.

3.0 COATING FORMULATION

The primer/topcoat development was completed in three phases. In the first phase, various polymeric binders were screened for adhesion, flexibility, chemical and weather resistance according to the methods previously described. Due to the stringent requirements for the desired coating, many resin systems were immediately eliminated from consideration. In general, epoxy polymers have poor weather resistance, alkyds do not have the required chemical or weather resistance, and acrylics lack adhesion, durability, and chemical resistance. Polyurethane resins were the primary binder candidates. After analyzing a number of polyurethane resins, the most promising material based on the above properties was a polyurethane which was obtained by reacting a blend of polyester polyols (X3009-Part A manufactured by Coatings for Industry) with hexamethylene diisocyanate (X3009 part B). Table I lists the resin characteristics and Figures 2 and 3 illustrate the infrared spectra of the two resins, respectively.

The objective of the second phase of the primer/topcoat development was to formulate a pigment system which would provide opacity, low gloss, corrosion protection, and a gray coating. The pigments also were evaluated for effects on coating flexibility and adhesion. This phase was performed by selecting and combining corrosion inhibitive, opaque, and extender pigments and incorporating them into the selected polyurethane resin at various concentrations. A theoretical prediction and statistically designed experimental verification approach outlined in references (2) and (3) was used to determine the most

likely optimum component concentrations and the compositions to be tested to verify these predictions. Since the objective was to develop white and camouflage gray coatings, candidate pigments had to be white, gray, or black. Extender pigments reduce gloss but provide little or no opacity to the dry film.

The most promising pigment system consisted of titanium dioxide, zinc phosphate, zinc molybdate, titanium dioxide vesiculated beads, and an organic zinc salt (SICORIN RZ manufactured by BASF). Titanium dioxide and titanium dioxide vesiculated beads are the primary pigments for providing opacity. The vesiculated beads also assist in reducing gloss due to their high oil absorption characteristics (2). Zinc molybdate, zinc phosphate, and Sicorin RZ are corrosion inhibitors. Table II lists the characteristics of these pigments.

After defining the binder/pigment system, the final phase of the development effort was completed by optimizing the solvent and pigment concentrations to obtain a material that exceeded the performance requirements of the primer (MIL-P-23377E) and the topcoat (MIL-C-83286B). The optimized composition of a lusterless white and a gray primer/topcoat along with critical compositional properties are provided in Table III. Physical and optical properties of these materials will be presented and discussed in the next section of this report. Initially, the candidate binder systems were thinned using solvents recommended by the polymer resin manufacturer. After it was determined that the X3009 polyurethane resin system manufactured by Coating For Industry was the prime candidate, Mil-T-81772, a standard urethane thinner, was used. In this final phase of development and optimization, 1,1,1 trichloroethane was substituted for the Mil-T-81772. This was done because 1,1,1 trichloroethane currently is an exempt solvent and thinning viscosity can be obtained without increasing the measured volatile organic content (VOC).

During the primer/topcoat development, it became apparent that the raw materials being used could also be applied to formulate flexible primers, with and without chromates. As a coinciding effort, an investigation was undertaken to develop these primers. Corrosion inhibiting pigments, including zinc chromate, strontium chromate, barium chromate, along with those previously identified, were combined with the x3009 polyurethane using an extreme vertices statistical design (4). The three critical properties evaluated were adhesion, flexibility, and corrosion inhibition. Table IV list the composition of the NADC flexible primer. The properties of this material are presented and discussed in the following section.

4.0 COATING TEST RESULTS AND DISCUSSION

The properties of the developed primer/topcoat and flexible primers are listed in Table V along with critical performance requirements of Mil-P-23377E epoxy primer and Mil-C-83286B topcoat.

4.1 Primer/Topcoat Analysis

From the data in Table V, it is evident that the primer/topcoat meets all of the critical requirements for both specifications. Although the Mil-C-83286B 60° gloss requirements for camouflage topcoats is 7 to 12, Navy aircraft are painted with a special designation Mil-C-83286B, "gunship quality" which has 60° and 85° gloss requirements of less than 3. Gloss is partially dependent upon

pigment milling and paint application procedures, therefore slight formulation modification may be necessary to obtain the desired gloss. The formulation concentrations listed in Table III are approximate and reduction of gloss may be accomplished by using a high oil absorption flattening agent such as amorphous silica. However, because addition of flattening agents also can cause loss in flexibility, large amounts of these agents are not recommended. In addition, it is believed that a 60° gloss of below 5 and an 85° gloss of below 10 are not significant increases and will not impact aircraft camouflage and vulnerability.

The specified exposure period for Mil-P-23377E and Mil-C-83286B on 2024-T3 in salt spray is 1000 and 500 hours, respectively. However, the primer/topcoat passed this requirement and the exposure period was continued for one year. Figure 4 is a photograph of Mil-P-23377E specimens, Figure 5 is Mil-P-23377E topcoated with Mil-C-83286B, and Figure 6 is the lusterless white primer/topcoat following 2000 hours in 5% salt spray. These specimens exhibited no substrate corrosion or blistering of the coatings. Figure 7 illustrates primer/topcoat specimens following one year in salt spray. Prior to chemically removing the coating in order to analyze the substrate, it was observed that the coating had blistered but was not punctured along the bottom edge of the exposed specimens and at one small area at the upper tip of one of the scribes. On both specimens, corrosion was observed at the areas where the coating had blistered. Due to the extent and location of the corrosion and the duration in salt spray, these results indicate good corrosion protection of the aluminum.

Yellowish deposits were observed in the circular corrosion areas and in the scribe as shown in Figures 9 and 10. These deposits are not grain-like as is usually observed with sodium chloride and aluminum oxide deposits. Chemical analysis of these deposits indicates a large concentration of aluminum and smaller concentrations of chromium, zinc, and molybdenum. Figure 10 is the scribe area of a primer/topcoat specimen after 2000 hours in salt spray. Although the deposits are present on the specimens, they do not cover the entire scribe area, indicating that a build-up of these deposits occurs with exposure in salt spray. Upon further examination, it was determined that there were no pits under these deposits in the scribe area. For comparison, Figure 11 is an NADC flexible primer specimen exposed to salt spray for one year which had no deposits in the scribe. The scribe area of this specimen was shiny, revealing the aluminum substrate.

The volatile organic content (VOC) of the primer/topcoat prior to thinning is 395 grams of organic solvent per liter of paint. After thinning to spray viscosity (20 - 22 seconds with a Zahn 2 cup) with 1,1,1 trichloroethane, which is currently an exempt solvent, the VOC of the primer/topcoat is 295 g/l. Currently, the most stringent solvent emission requirements are set by the South Coast Air Quality Control District in California. The limitations for topcoats are 420 g/l for aerospace equipment and 350 g/l for miscellaneous metal parts. The primer/topcoat meets both of these regulations and has the added advantage of not requiring a primer coat, further minimizing solvent emissions.

As stated previously, adhesion, flexibility, strippability, corrosion resistance, fluid resistance, heat resistance, and weatherability of the primer/topcoat meet or exceed the appropriate primer and topcoat specification requirements. The benefits of this material are:

1. Decreased paint application time and manpower

2. Less applied paint and lower aircraft weight
3. Reduced aircraft downtime
4. Less volatile organic solvent emissions
5. No chromate emissions

The cost of aircraft painting and stripping subsequently can be reduced due to less manpower and material requirements. Lower VOC and the absence of chromates in the coating are beneficial for worker safety and environmental concerns which also lessens the burden on painting facilities such as NARFs and OEMs in conforming with emission regulations.

4.2 NADC Flexible Primer Analysis

The NADC flexible primer meets or exceeds all the requirements of Mil-P-23377E except the set-to-touch time which is less than 30 minutes; the flexible primer is set-to-touch in less than 45 minutes. This is not considered significant because the set-to-touch and dry hard times of the flexible primer are far less than that for the topcoat, which would normally be applied over the primer. Therefore, the additional 15 minutes required for the set-to-touch time for the flexible primer would not add a significant amount of time to apply the entire coating system to an aircraft. It should also be noted that the polyurethane binder system of this flexible primer is similar to that of the MIL-C-83286. Overcoating with MIL-C-83286 shortly after application of this primer will improve the intercoat adhesion of the paint system. The main reason for delay between priming and topcoating is to allow most of the primer solvent to evaporate. This will occur within 30 minutes.

One objective in developing this coating was to meet the requirements for a proposed specification for a flexible primer (Table VI). To date, the only material known to meet these requirements is Koroflex (DeSoto, Inc.). The NADC flexible primer meets or exceeds all of these requirements except elongation at break. The elongation at break of the NADC primer is 31%. Although this is significantly less than the 100% requirement, the flexibility required of a primer to prohibit coating failure on an aircraft is unknown. Koroflex has performed well in field tests on operational aircraft. Field testing of the NADC primer is currently being performed to determine if its flexibility is adequate to significantly reduce cracking of the aircraft paint system. Increasing the flexibility of the NADC primer may be possible by blending the polyurethane binder with a more flexible resin and by incorporating elastomeric fillers into the coating. Both of these techniques would cause the addition of elastomeric domains in the cured coating which would relieve stresses, prohibiting cracking of the coating (5).

The corrosion properties of the NADC flexible primer are notable. Figures 12 and 13 illustrate the NADC primer with and without a topcoat after 2000 hours in salt spray. Figure 14 illustrate Koroflex specimens after 2000 hours salt spray. All of the specimens had no corrosion of the substrate or uplifting of the coating. Figure 14 shows some surface staining of the Koroflex due to inadvertent splashing of a contaminant; however, no damage of the coating was observed. Figure 15 illustrates the NADC flexible primer after 1 year exposure to 5% salt spray. There was no corrosion or uplifting and the scribe area was shiny, indicating excellent corrosion inhibition. Figure 11 further illustrates the corrosion protection provided by the NADC flexible primer.

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The corrosion inhibiting pigments utilized in the flexible primer, as indicated in Table IV, are a combination of strontium chromate, barium chromate, zinc chromate, and zinc molybdate. These pigments and their concentrations were determined using a statistical experimental design to determine the most effective inhibiting system for this primer. It must be noted that in the X3009 polyurethane resin system, this exact pigment formulation provided corrosion protection superior to any single pigment, including strontium chromate.

A second objective in the primer formulation effort was to develop a non-lead, non-chromate primer for aluminum which will provide all of the desired properties, especially corrosion inhibition. It is obvious from the primer/topcoat formulation that non-lead, non-chromate, corrosion preventive coatings for aluminum can be developed. Currently, there are two military specifications, Mil-P-52995 and Mil-P-53030, for lead and chrome free corrosion preventive primers for ferrous and non-ferrous substrates. The pigment system in these primers contains iron oxide, zinc phosphate, and Sicorin RZ. Mil-P-52995 is a phthalic alkyd binder and Mil-P-53030 is an epoxy binder. Several preliminary in-house primers were developed which had fair corrosion protection. This investigation is continuing in order to develop an optimum coating without lead or chrome pigments.

The VOC of the NADC flexible primer is 442 g/l prior to thinning and 294 g/l after thinning to spray viscosity with 1,1,1 trichloroethane. The current South Coast Air Quality Control District Regulations for primers are 350 g/l for aerospace equipment and 340 g/l for metal parts. The thinned flexible primer meets both of these requirements.

5.0 CONCLUSIONS

A coating has been developed which can be applied directly to an aluminum substrate and provide the properties of both a primer and a topcoat. This coating meets all of the critical performance requirements of the primer and topcoat currently used on Navy aircraft. The primer/topcoat coating provided corrosion protection for an aluminum substrate for over 2000 hours in salt spray with a non-lead and non-chrome pigment system. When used to replace the primer and topcoat coating system on Navy aircraft, the primer/topcoat will reduce paint application cost and time, aircraft downtime, and volatile organic and chromate emissions.

A flexible primer has been developed which meets the requirements for Mil-P-23377E. This primer also passes all of the requirements of a proposed flexible primer specification except elongation at break. It does pass other stringent low and ambient temperature flexibility requirements.

6.0 FUTURE EFFORTS

Field tests on operational F-14 aircraft are planned for the primer/topcoat and flexible primer discussed in this report. These coatings also are being analyzed in the laboratory for their performance on graphite/epoxy composites common on tactical military aircraft. Additional coating development is being performed to obtain a non-lead, non-chrome primer for aluminum and to develop a more flexible primer.

7.0 REFERENCES

1. D. F. Pulley and S. J. Spadafora, "Elastomeric Primers and Sealants", Naval Air Development Report NADC-83140-60, Warminster, PA, November 1983.
2. C. R. Hegedus and A. Eng, "Optimization of Binary Pigment Coatings", NADC Report In Publication
3. C. R. Hegedus and P. G. Prale, "Polymer Bead Pigments in Aircraft Coatings", NADC-85025-60, Warminster, PA, March 1985.
4. R. A. McLean and V. L. Anderson, Technometrics, Vol. 8, No. 3, 447-454, August 1966.
5. J. A. Manson and L.H. Sperling, POLYMER BLENDS AND COMPOSITES, Plenum Press, New York, 1976.

8.0 ACKNOWLEDGEMENT

The author wishes to thank Mr. William Green for performing the coating tests and assisting in the evaluations during this effort. The author also wishes to acknowledge Mr. Jim Klotz of Coatings For Industry, Inc. for our interesting discussions and the numerous samples which he provided during this effort.

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Table I: Characteristics of Polyurethane Resin X3009.

X3009 Component A

Percent Solids	46.2
Hydroxyl Number	71
Acid Number	9
Average Equivalent Weight	790
Density	1.06

X3009 Component B

Percent Solids	75.4
Percent Isocyanate (NCO) Content	16.5
Average Equivalent Weight	253
Density	1.07

Table II: Properties of Pigments

	<u>Titanium Dioxide</u>	<u>Zinc Molybdate</u>	<u>Zinc Phosphate</u>	<u>Sicorin RZ</u>	<u>TiVs90</u>
Appearance	White	White	White	White	White
Shape	Spherical	Spherical	Rectangular	Platelet	Spherical
Density (g/ml)	4.0	5.0	3.6	2.5	0.6
Oil Absorption (ASTM D281)	29.3	16.0	23.2	57.2	146.8
Particle Size, Average, in microns	0.2	4.0	6.0	2.5	5.0

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Table III: Composition of Lusterless White Primer/Topcoat

Component A	Percent by Weight
X3009 A	37.8
Titanium dioxide	1.1
Titanium dioxide ves. bds.	0.4
Zinc Phosphate	17.1
Sicorin RZ	1.7
Zinc molybdate	<u>30.1</u>
Sub-total	88.2

Component B

X3009B	<u>11.8</u>
Total	100.0

These materials are mixed approximately 4 parts of Component A to 1 part of Component B by volume. 26 grams (20 milliliters) of 1,1,1 trichloroethane were added to obtain a spray viscosity of 20 to 22 seconds using a Zahn 2 cup.

Pigment* Volume Concentration	33.3
Pigment-To-Binder Ratio	1.9
Wet Density (g/ml)	1.7
Dry Density (g/ml)	2.1
Volatile Organic Content (g/liter of paint)	
After thinning with 1,1,1 trichloroethane	295
Prior to thinning	395

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Table IV: Composition of NADC Polyurethane Flexible Primer

Component A	Weight Percent
X3009-A	53.2
Strontium chromate	4.4
Zinc chromate	4.4
Barium chromate	5.0
Zinc molybdate	5.4
Titanium dioxide	3.1
Magnesium silicate	5.6
Sub-total	81.1
Component B	
X3009-B	18.9
Total	100.0

These materials are mixed approximately 4 parts of Component A to 1 part of Component B by volume. 40 grams (37.8 milliliters) of 1,1,1 trichloroethane were added to obtain a spray viscosity of 20 to 22 seconds using a Zahn 2 cup.

Pigment Volume Concentration	20.4
Pigment-To-Binder Ratio	.7
Wet Density (g/ml)	1.3
Dry Density (g/ml)	1.6
Volatile Organic Content (g/liter of paint)	
After thinning with 1,1,1 trichloroethane	294
Prior to thinning	395

Table V: Mil-P-2337E and Mil-C-83286B Requirements and Primer/Topcoat and Flexible Primer Properties.

COILING PROPERTIES	MIL-P-2337E PRIMER REQUIREMENTS	MIL-C-83286B TOPCOAT REQUIREMENTS	PRIMER/TOPCOAT PROPERTIES	FLEXIBLE PRIMER PROPERTIES
Set-to-touch time (hour)	≤ 0.5	≤ 2	≤ 0.75	≤ 0.75
Dry hard time (hour)	≤ 6	≤ 6	≤ 3	≤ 3
60 gloss	≥ 10	Camouflage ≤ 12 & ≥ 7	≤ 3	≤ 10
65 gloss	--	--	≤ 3	--
Adhesion - wet tape test	No uplifting, SA	No uplifting, SA	No uplifting, SA	No uplifting, SA
Adhesion - scrape test (kg)	≥ 3	--	3	3.5
Flexibility - impact (% elongation)	≥ 60	Camouflage ≥ 20	20	60
Flexibility - standard bend	--	Camouflage ≤ 0.5 inches	0.125 inches	0.125 inches
Stripability (% surface area stripped)	≥ 90	--	100	100
Water resistance	No coating defects	No coating defects	No coating defects	No coating defects
Corrosion - salt spray aluminum	No substrate corrosion or coating blisters	No substrate corrosion or coating blisters	No substrate corrosion or coating blisters	No substrate corrosion or coating blisters
aluminum/composite	No pitting greater than line in depth	--	No substrate corrosion or coating blisters	No substrate corrosion or coating blisters
Corrosion - filiform	No filiform corrosion en- tailing beyond 0.25° from scribe and majority of fill- ments less than 0.125°	--	Pass Mil-P-2337E requirements	Pass Mil-P-2337E requirements
Fluid resistance Mil-L-23599	No coating defects	No coating defects	No coating defects	No coating defects
Mil-H-5606	No coating defects	No coating defects	No coating defects	No coating defects
Mil-H-83282	No coating defects	--	No coating defects	No coating defects
Mil-H-83306 (Sdy. 5008)	--	No coating defects	No coating defects	No coating defects
Humidity resistance	--	No coating defects	No coating defects	No coating defects
Heat resistance	--	Maintain gloss, color and flexibility requirements	Pass Mil-C-83286B requirements	--
Accelerated weathering	--	Maintain gloss, color, and flexibility requirements	Pass Mil-C-83286B requirements	--

Table VI: Proposed Flexible Primer Specification Requirements

<u>COATING PROPERTIES</u>	<u>PROPOSED REQUIREMENT</u>
60° gloss	20
Adhesion - wet tape test	No uplifting
Adhesion - scrape test	2 Kg
Impact flexibility	60% elongation
Handrel bend @ -60F	0.125 inches
Tensile strength	2500 PSI
Elongation at break	100%
Water resistance	No coating defects
Humidity resistance	No coating defects
Mil-L-23699 resistance	No coating defects
Mil-H-83282 resistance	No coating defects
Corrosion - salt spray Aluminum	No corrosion or blistering
Aluminum/graphite	No pitting greater than 1 mm in depth
Corrosion - filiform	No filiform extending beyond 0.25" from scribe and majority of filament less than 0.125"
Solvent resistance	No coating removal
Strippability	90% surface area stripped

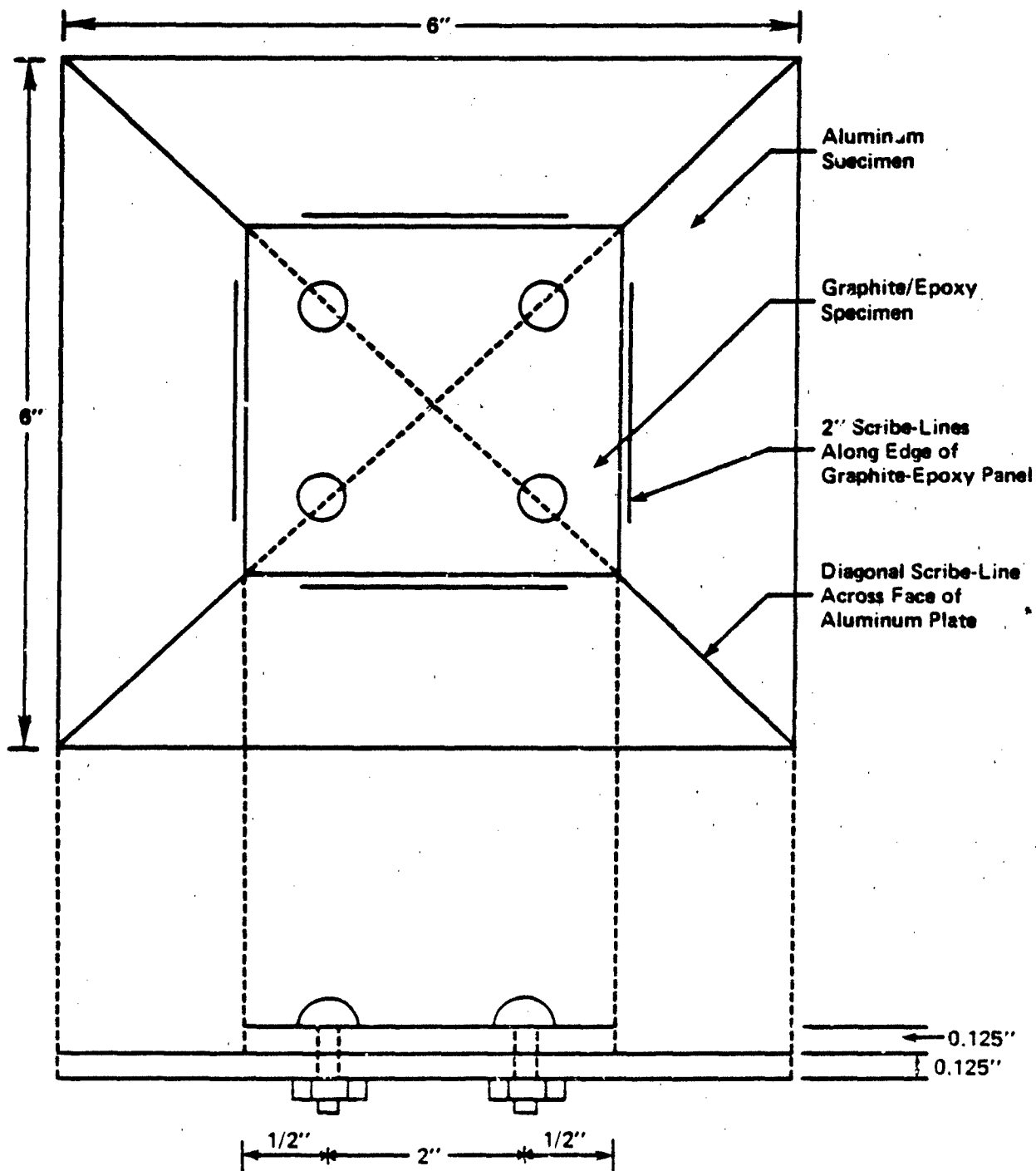


Figure 1: Aluminum/Graphite-Epoxy Corrosion Test Specimen

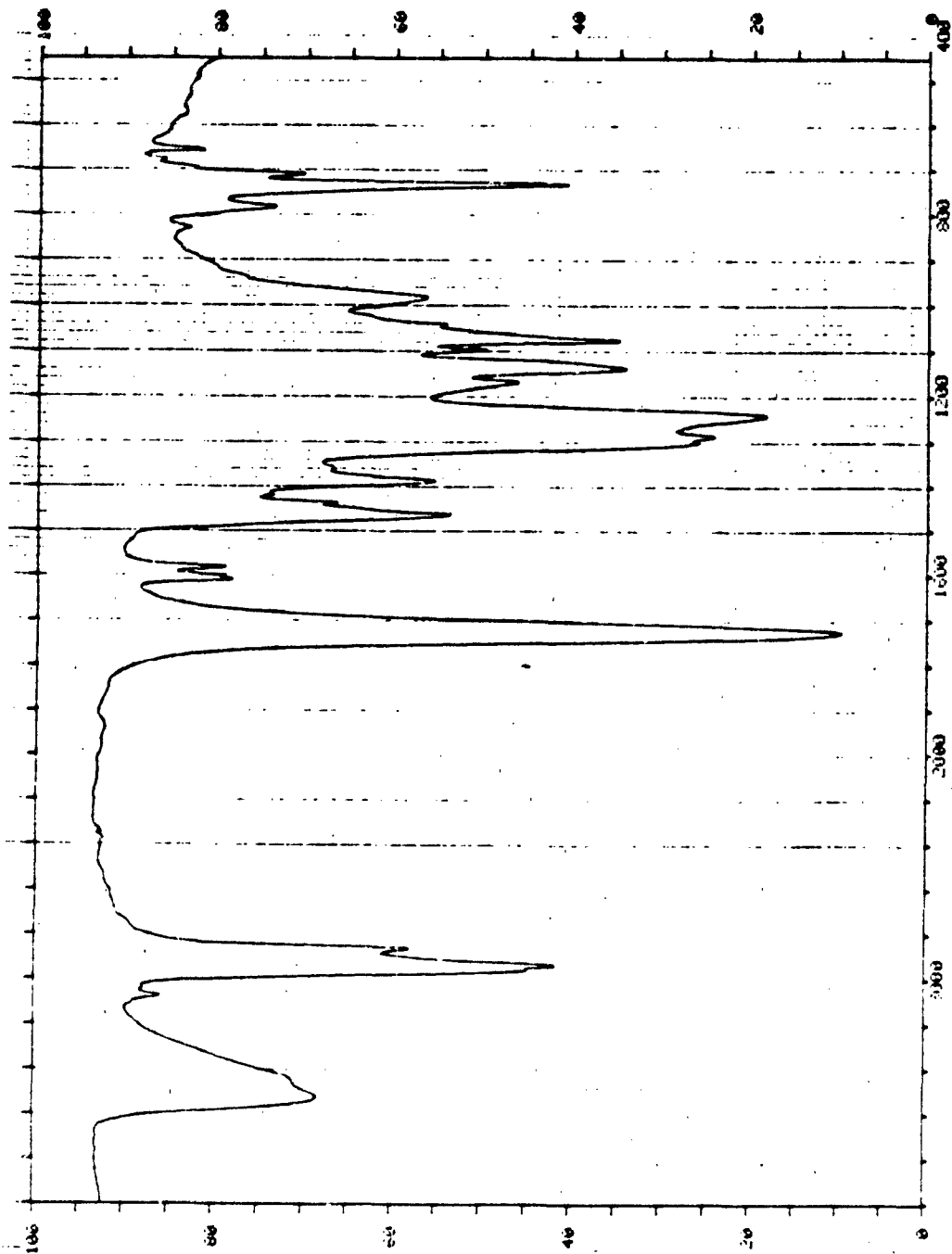


Figure 2: Infrared Spectra of X3009, Part A, Polyester Polyol

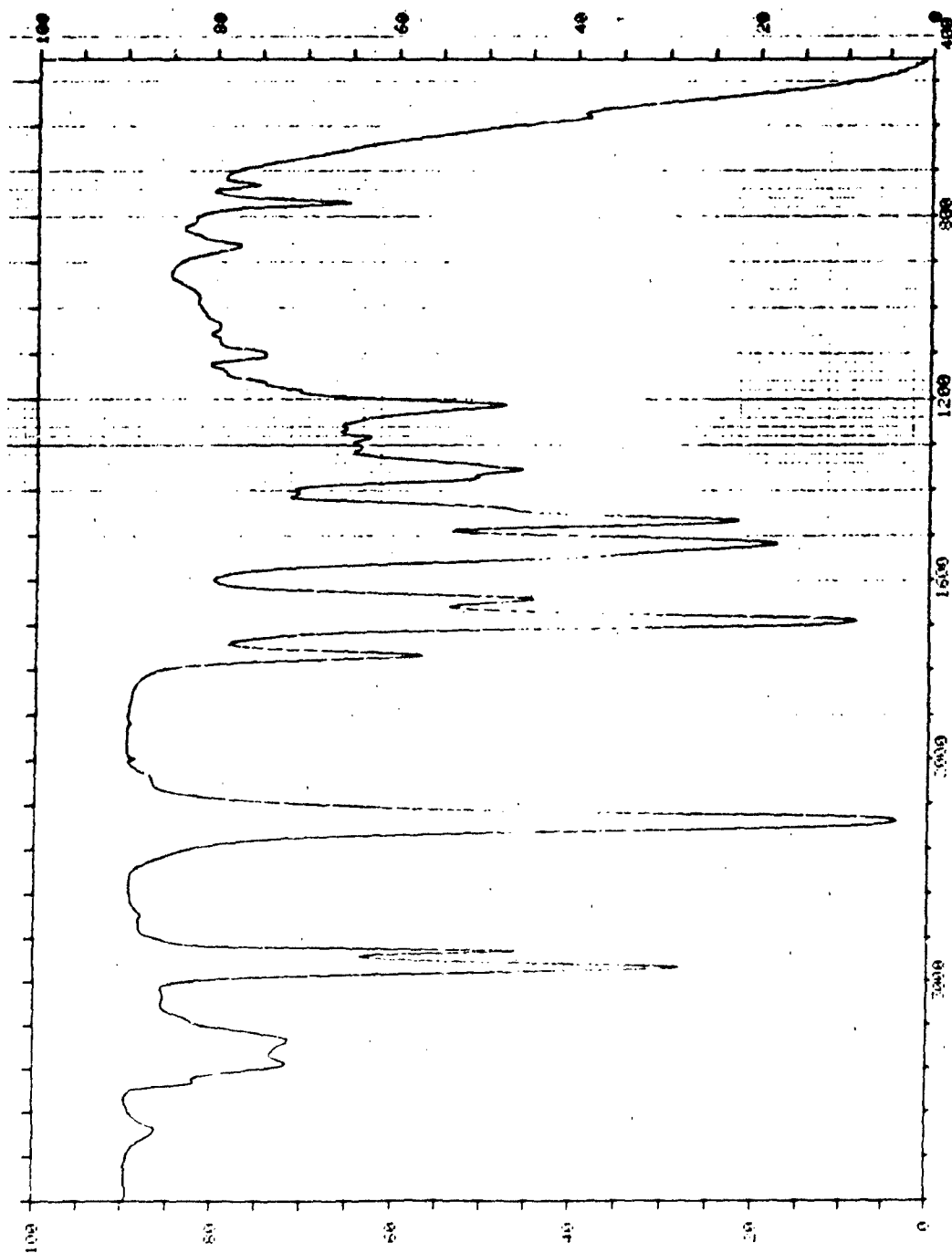
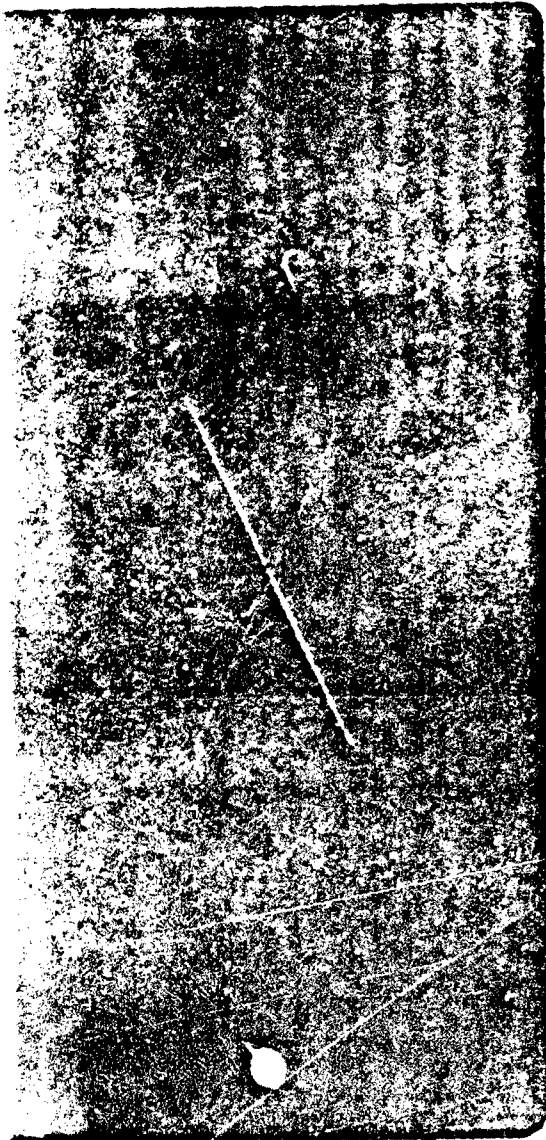


Figure 3: Infrared Spectra of X3009, Part B, Hexamethylene Diisocyanate

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2000 HOURS SALT SPRAY



AFTER EXPOSURE



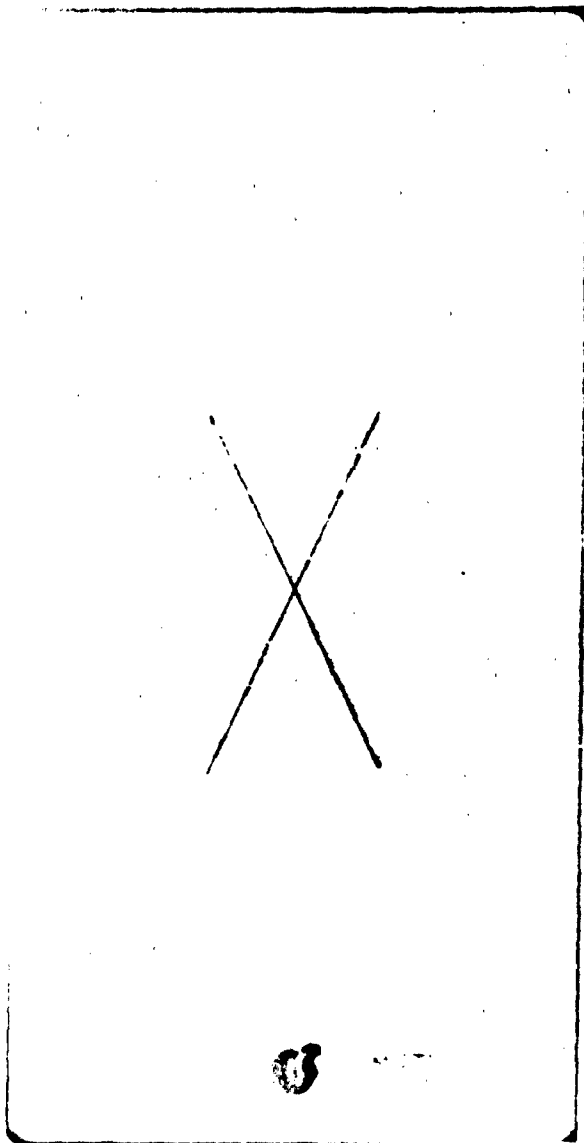
COATING REMOVED

MIL-P-23377E

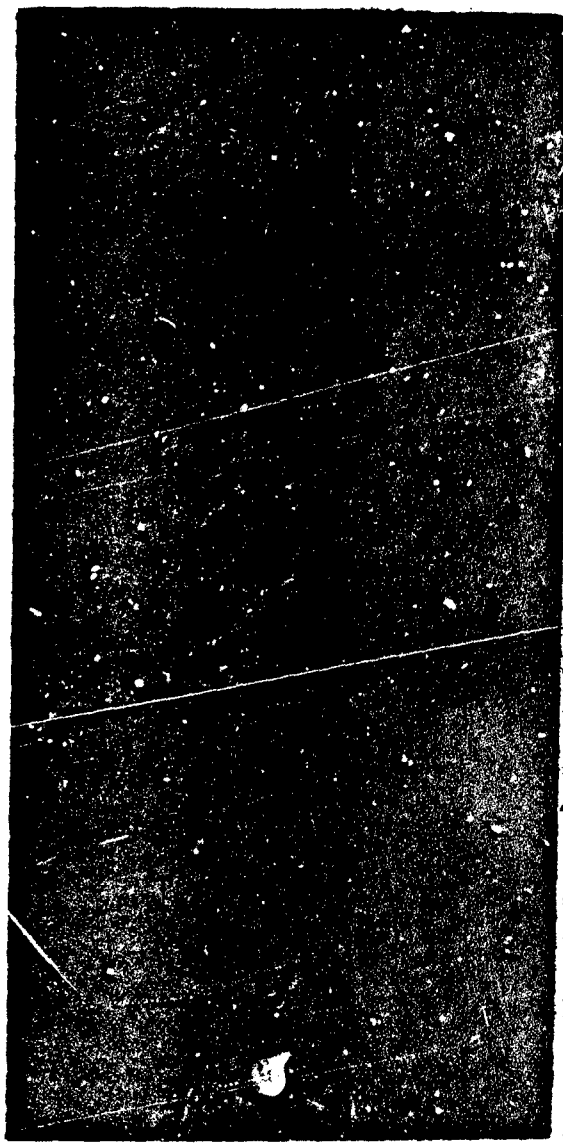
Figure 4: MIL-P-23377E Exposed to Salt Spray for 2000 hours

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2000 HOURS SALT SPRAY



AFTER EXPOSURE



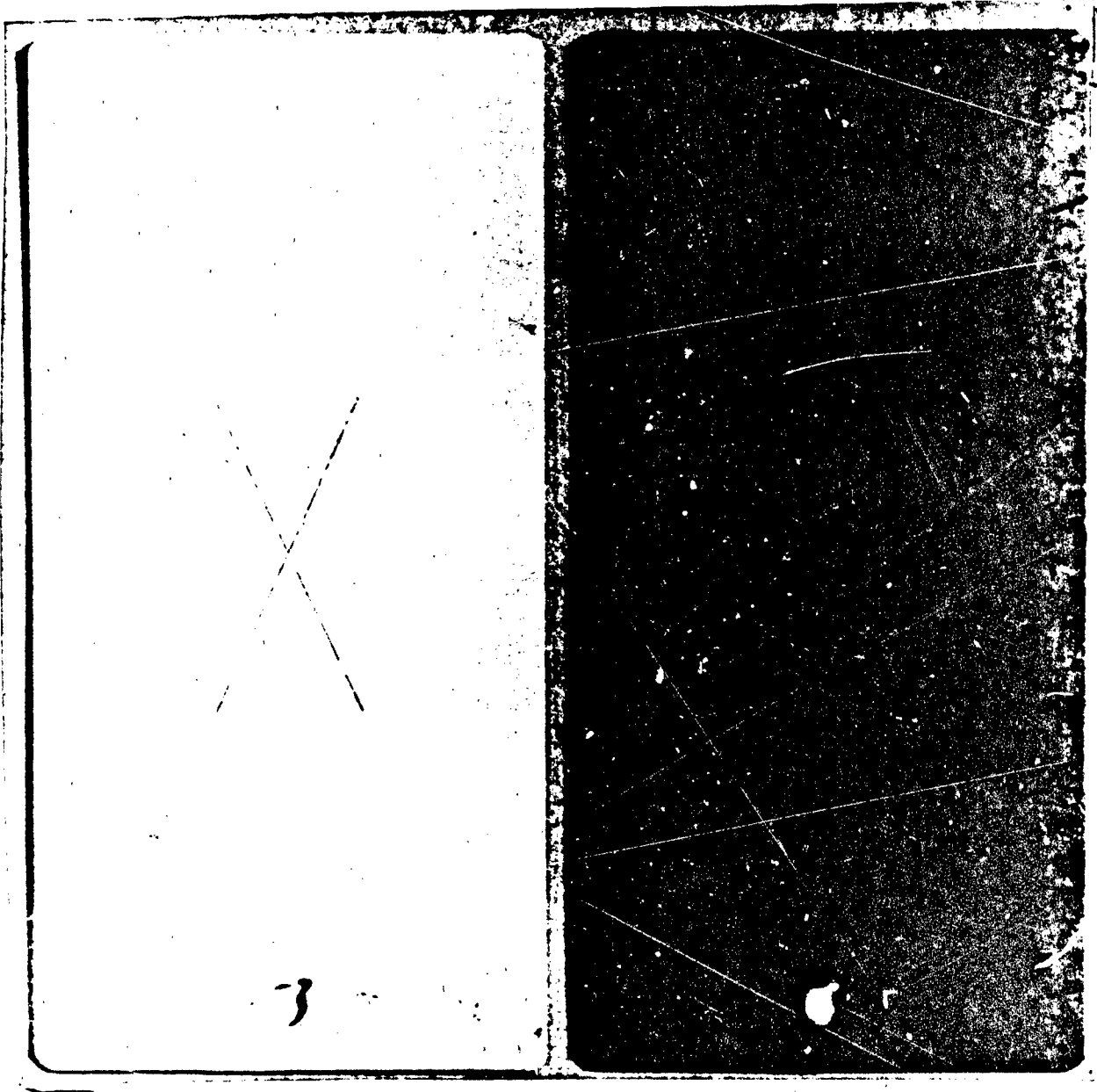
COATING REMOVED

MIL-P-23377E/MIL-C-83286B

PLATE 5: MIL-PRC-23377E/MIL-C-83286B

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2000 HOURS SALT SPRAY



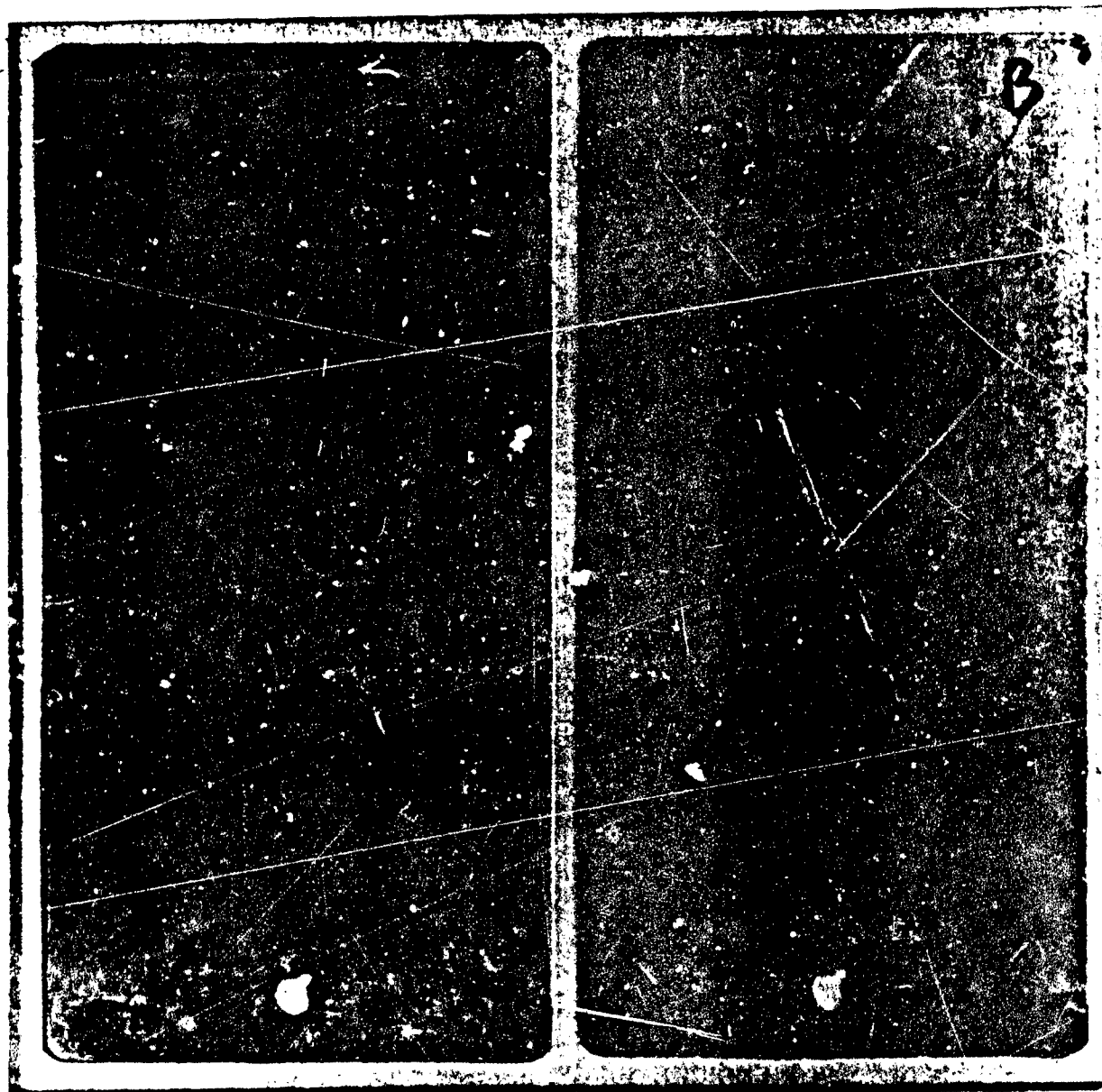
AFTER EXPOSURE

COATING REMOVED

PRIMER/TOPCOAT

Figure 6: Primer/Topcoat Specimens Exposed to Salt Spray for 2000 Hours

ONE YEAR SALT SPRAY



COATING REMOVED

PRIMER/TOPCOAT

Figure 7: Primer/Topcoat Specimens Exposed to Salt Spray for One Year



**FIGURE 8: CIRCULAR AREA ON PRIMER/TOPCOAT SPECIMEN
EXPOSED TO SALT SPRAY FOR ONE YEAR (20X)**

← 1mm →

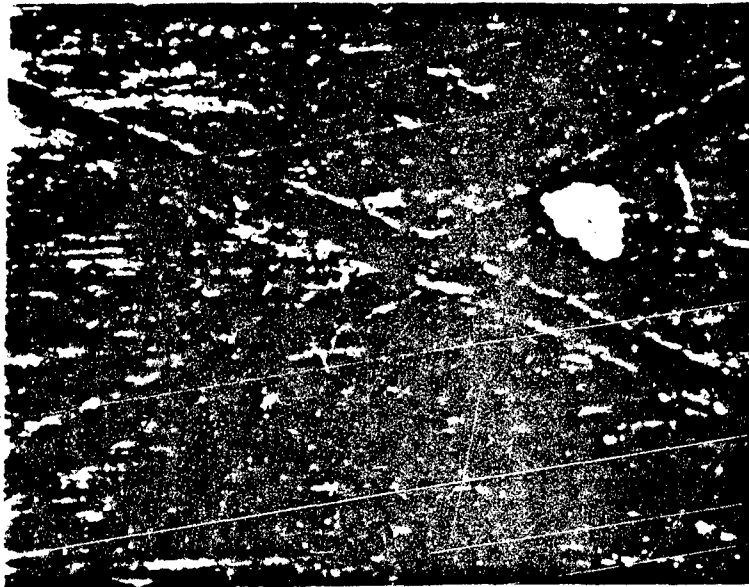


**FIGURE 9: SCRIBE AREA ON PRIMER/TOPCOAT SPECIMEN
EXPOSED TO SALT SPRAY FOR ONE YEAR (20X)**



**FIGURE 10: SCRIBE AREA ON PRIMER/TOPCOAT SPECIMEN
EXPOSED TO SALT SPRAY FOR 2000 HOURS (20X)**

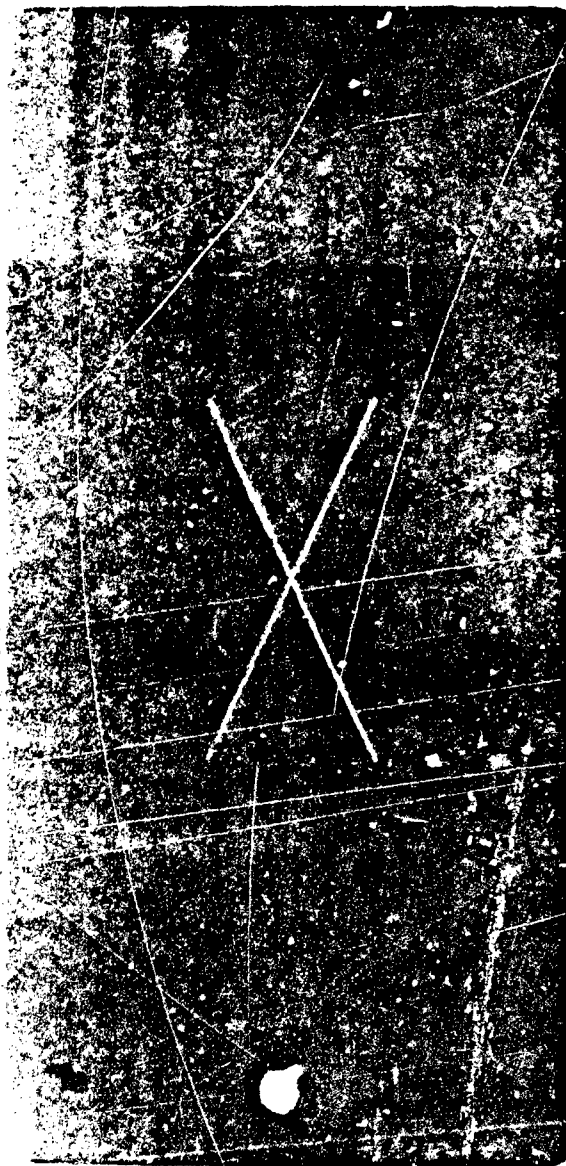
— 1mm —



**FIGURE 11: SCRIBE AREA ON THE NADC FLEXIBLE PRIMER
EXPOSED TO SALT SPRAY FOR ONE YEAR (20X)**

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2000 HOURS SALT SPRAY



AFTER EXPOSURE

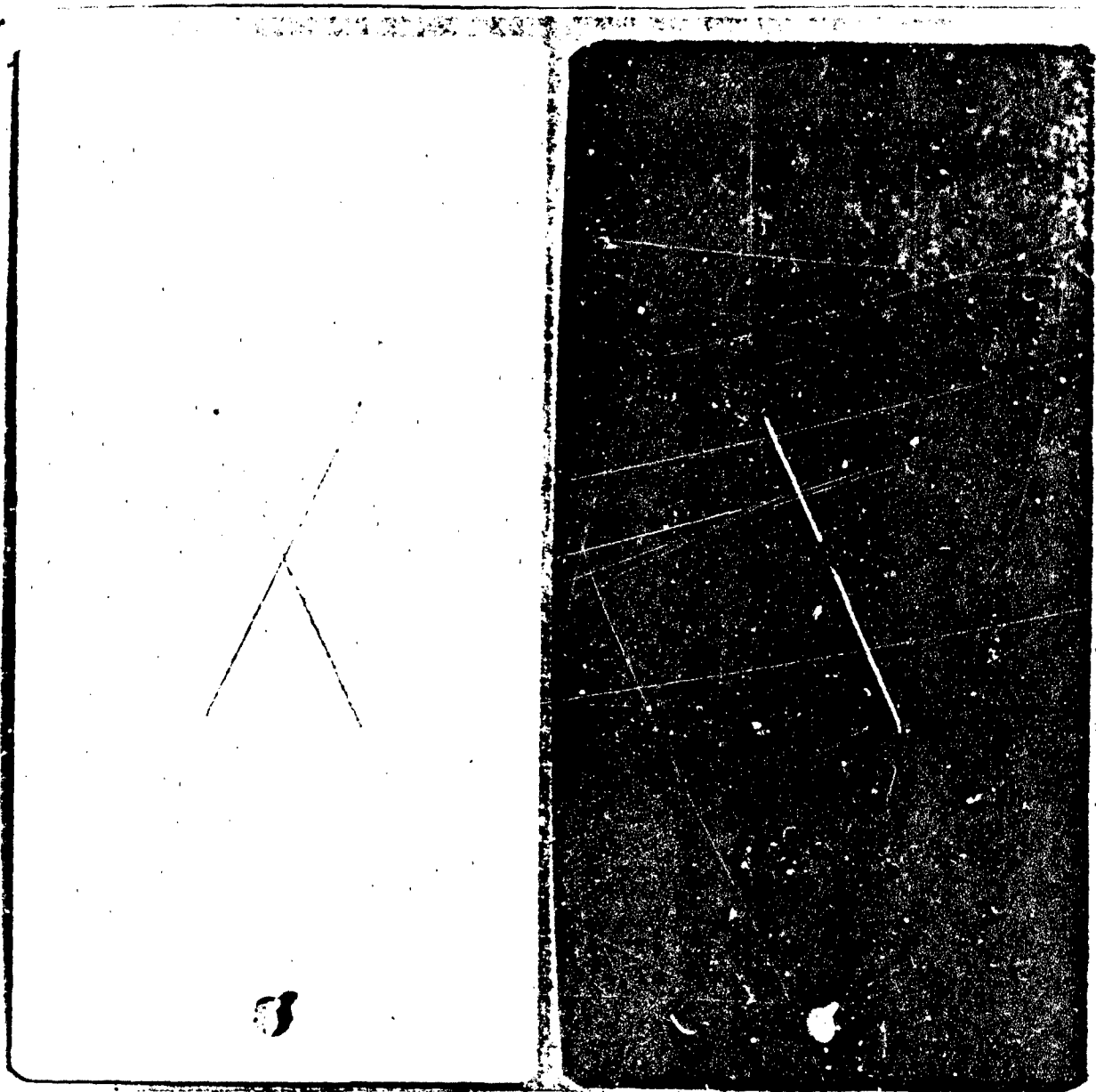


COATING REMOVED

NADC FLEXIBLE PRIMER

Figure 12: NADC Flexible Primer Exposed to Salt Spray for 2000 Hours

2000 HOURS SALT SPRAY



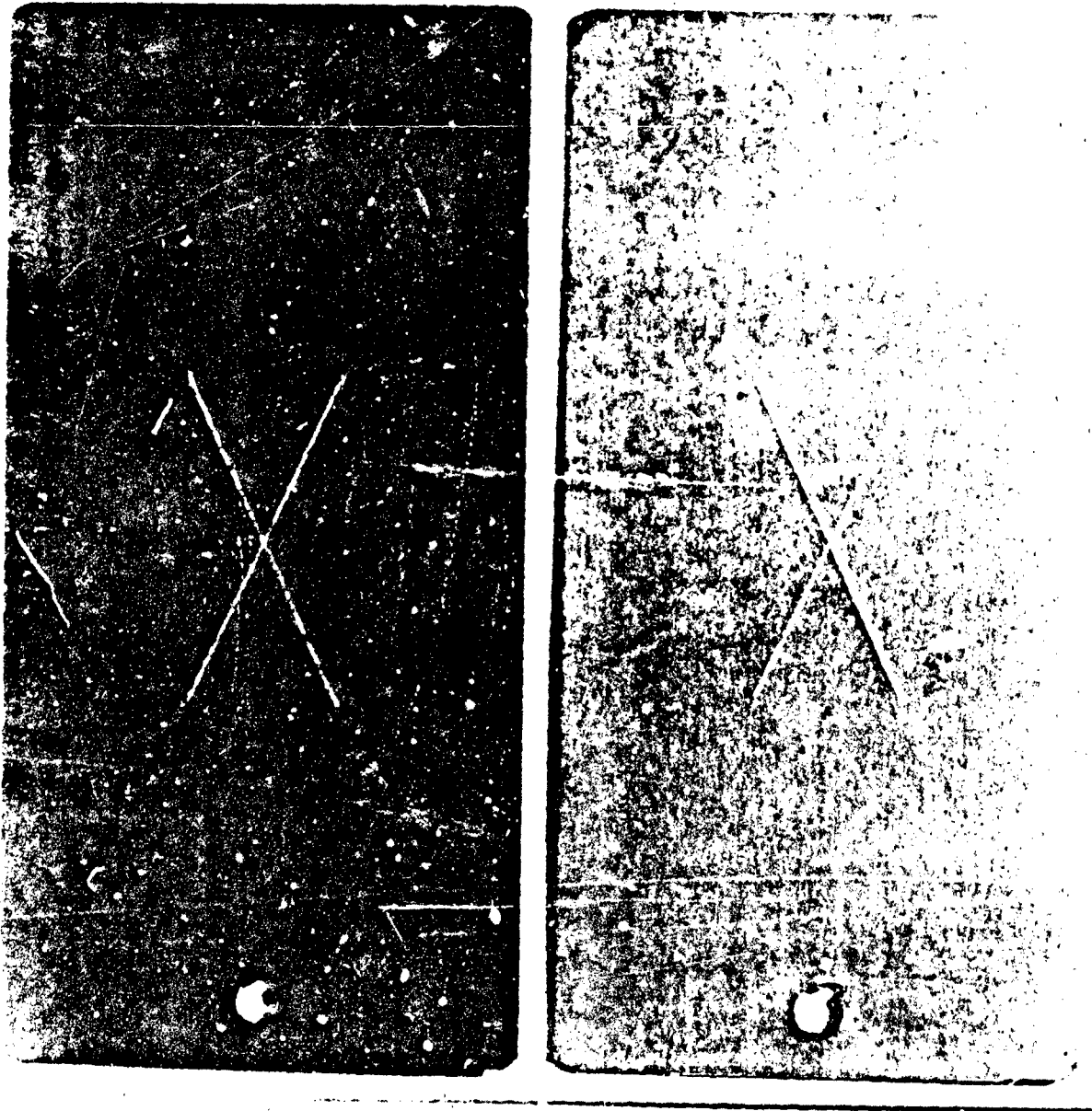
AFTER EXPOSURE

COATING REMOVED

NADC FLEXIBLE PRIMER/MIL-C-83286B

Figure 13: NADC Flexible Primer/MIL-C-83286 Exposed to Salt Spray for One Year

2000 HOURS SALT SPRAY



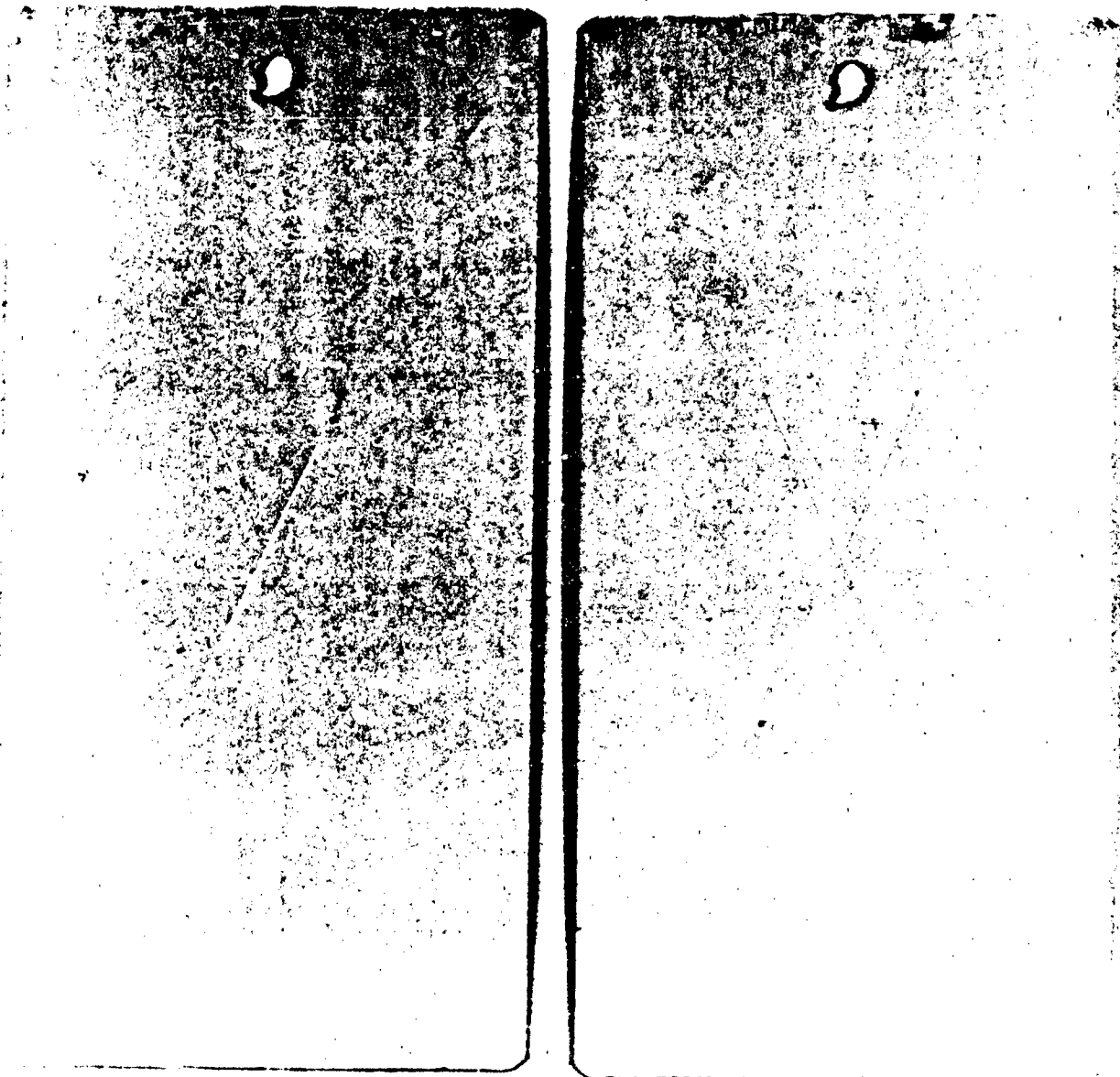
AFTER EXPOSURE

COATING REMOVED

KOROFLEX PRIMER

Figure 14: Koroflex Primer Exposed to Salt Spray for 2000 Hours

AFTER 1 YEAR 5% NaCL EXPOSURE



COATING REMOVED

Figure 15: NADC Flexible Polymer Exposed to Salt Crystals for one year.

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